



Influence of reaction atmosphere and solvent on biochar yield and characteristics



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HIGHLIGHTS

- Influence of solvents on the production of biochar is explained.
- Influence of reducing and non-reducing atmospheres in biochar yield is explained.
- Comprehensive analyses of the biochar explains the reaction yields obtained.
- First results on biochar produced from sunflower husks via thermochemical liquefaction.

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ABSTRACT

Sunflower husks were converted to biochar via thermochemical liquefaction in different solvents and reaction atmospheres. Highest biochar yields obtained was 574 g kg^{−1} husks. Surface area of the produced chars and evolution of aromatic compounds in the biochar structure increased with an increase in temperature. Volatile matter and N-content decreased and S-content decreased significantly with an increase in temperature which is favourable should the biochars be used for combustion. The HHV of the biochars were significantly higher than that of the feedstock as was also indicated by the energy densification ratio. The biochars compared favourable with coal on a Van Krevelen diagram, showing the possibility of the biochars for application in co-gasification. CO₂ performed better in retaining the energy of the feedstock in the biochar (up to 58%). It was shown that sunflower husks are a viable feedstock for the production of biochars for application in co-gasification or combustion.

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1. Introduction

Biochar is a coal like substance produced as the solid fraction during liquefaction or pyrolysis of biomass materials. It is usually porous with oxygen functional groups and an aromatic surface which makes it an ideal adsorbent for heavy metals and non-polar organic substances (Ghani et al., 2013; Yu et al., 2012). High pyrolysis temperatures (>550 °C) leads to the destruction of the phenolic bonds associated with lignin and this may lead to increased cross-linking between aromatic rings and other hydrocarbons present, which results in the formation of heavy tars (Liu et al., 2006). One of the largest benefits of liquefaction over pyrolysis is the absence of tars formation during the relatively mild thermal treatment. Bio-based products produced via liquefaction generally has a lower oxygen content and a higher calorific value than those produced through fast pyrolysis (Brand et al., 2013), making

liquefaction the preferred process for the production of biochars with a high energy value.

Liquefaction removes oxygen from the biomass material through a combination of dehydration, decarbonylation and decarboxylation reactions. The cellulose and hemicellulose components of the biomass are mostly converted to sugars which further decompose and polymerise to form bio-oil, biochar and gas (Choudhary and Philips, 2011). Hemicellulose is decomposed first, followed by cellulose and lignin with increasing temperature. Rapid removal of cellulose and hemicellulose at relatively low carbonisation temperatures will increase the biochar yield as well as the higher heating value of the char (Lyman et al., 2012). Biomass containing high amounts of lignin has been associated with high biochar yields from thermochemical liquefaction (Akhtar and Amin, 2011). Phenolic compounds associated with the liquefaction of lignin are attractive for the production of a wide range of bio-based chemicals such as phenolic precursors, polymers and aromatics (Xiao et al., 2012).

Various process parameters that influence biochar production from a variety of biomass feedstock have been investigated in

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literature. It has been shown that an increase in temperature results in a decrease in solid char yield and in increase in fixed carbon content of biochars while a decrease in oxygen and hydrogen content through the carbonisation reaction path is observed (Liu et al., 2013a,b; Roman et al., 2012; Lu et al., 2012). An increase in biomass loading (thus less water and/or solvent present) leads to a decrease in biochar yield (Roman et al., 2012). Residence time does not seem to have a significant influence on the overall biochar yield, irrespective of the biomass feedstock used, with residence times ranging from 15 min to 4 h. Reaction atmosphere have not been widely investigated, but Lu et al. (2012) showed that a nitrogen atmosphere during hydrothermal liquefaction of oil palm fibre and eucalyptus generally result in a char with a higher fixed carbon and lower ash content than chars prepared in air. The influence of reaction atmosphere on the properties of biochar seems to be related to the original composition of the biomass feedstock, with feedstock with a higher hemicellulose content being more greatly and positively influenced by a reducing atmosphere than feedstock with high cellulose content. Changes in the H/C and O/C ratio of biomass feedstock during thermal treatment are associated with demethanation, dehydration and decarboxylation reactions with the O/C ratio directly linked to the decarboxylation of the biomass (Parshetti et al., 2013; Sevilla and Fuertes, 2009; Sevilla et al., 2011). Water is the solvent of choice for most thermochemical liquefaction studies for biochar production and to the author's knowledge, no publication on the influence of solvents on biochar yield and characteristics have been published to date. The role of the solvent during treatment is usually to fragment the biomass and stabilise the fragmented products to ensure maximum production of bio-oil. The better the solvent is at stabilising the fragments, the higher the oil yield and the lower the solid biochar fraction (Akhtar and Amin, 2011). It thus follows that solvents that tend to increase the fragmentation of the biomass and disrupts the stability of the reaction mixture should increase the solid biochar yield.

In this study, the influence of reaction atmosphere and solvent on the production of biochar from sunflower husks was investigated. A reducing atmosphere (N_2) and a non-reducing atmosphere (CO_2) was used in the presence of different solvents such as water and alcohols of different carbon chain lengths to assess the influence of these parameters on the biochar yields as well as the characteristics of the chars produced.

2. Methods

2.1. Materials

Sunflower husks were obtained from a sunflower oil processing facility near Lichtenburg in the North West Province of South Africa (26°09'S 26°10'E). A single batch of husks from a single harvest was used in all experiments. The husks were transported from the oil processing facilities in Hessian bags to the laboratories of the North-West University in Potchefstroom, South Africa. The husks were stored in the bags in a temperature controlled environment at 20 °C for the duration of the experiments. The husks were washed

as part of the processing steps at the oil processing facility and thus were not pretreated or washed prior to use in the experiments.

Nitrogen (N_2) (ultra high purity) and carbon dioxide (CO_2) (technical grade) was obtained from Afrox gas company. Solvents used in this study were all of 99% purity and were obtained from Rochelle Chemical Company. Solvents were used as received without prior purification. The solvents with some properties are listed in Table 1.

As the number of carbon atoms in the solvent increase, so does the boiling point while the dielectric constant and dipole moment decreases. Molecules with a permanent polar charge has a dipole moment and the higher the number, the more polar the molecule is. The dielectric constant of a molecule gives an indication of the degree to which the molecule can be polarised in the right circumstances. The higher the dielectric constant, the more easily the molecule will be polarised.

2.2. Compositional analysis of sunflower husk feedstock

The moisture content of the husks were determined to be 10 wt.% as loss of drying for 24 h at 105 °C in an incubator oven. A proximate analysis of the husks was done using thermogravimetric analysis (TGA) (U-Therm-system, China). Samples were heated up to 105 °C at a rate of 10 °C/min then up to 900 °C at a rate of 50 °C/min. Mass evolved at 105 °C was taken to be moisture, while mass evolved between 105 and 900 °C was taken to be volatiles (14.16 wt.%). All mass remaining after heating to 900 °C consisted of fixed carbon (71.24 wt.%) and ash (4.6 wt.%). Composition analysis of the sunflower husks used in this study was done by the laboratories of the Agricultural Research Council (ARC) at Irene, South Africa and the results are presented in Table 2.

Protein content in the sample was determined by the Kjeldahl method which measures total organic nitrogen. The organic matter was digested with concentrated sulphuric acid and the catalyst mixture was added to raise the boiling point. All nitrogen was converted to ammonia which was measured by titration. Acid detergent fibre (ADF) content was determined by heat treatment of the sample with sulphuric acid containing cetyltrimethyl ammonium bromide (Goering and Van Soest, 1970). The difference in NDF and ADF values gave an estimation of the content of non cellulose polysaccharide. The ADF residue mainly contains cellulose and lignin. The lignin content was determined by permanganate oxidation and the resulting residue gave the lignin content. The lignin content of sunflower husks is high compared to woody and grass type biomass and compares to the lignin content of most nutshells (Abbasi and Abbasi, 2010). High lignin content in a biomass feedstock is associated with a high higher heating value (HHV) (Novaes et al., 2010) and thus it is expected that sunflower husks will yield biochars with high energy content.

2.3. Liquefaction system and experimental procedure

Liquefaction experiments were carried out in a standard SS316 stainless steel high-pressure autoclave (Sawayama et al., 1995;

Table 1
Some properties of solvents used in this study.

Solvent	Density ($kg\ m^{-3}$) ^a	Boiling point (K) ^b	Critical temperature (K)	Critical pressure (MPa)	Dielectric constant	Dipole Moment
Water (distilled)	1000	373	647	22	78.54	1.85D
Methanol	791	338	512	6.4	32.6	1.70D
Ethanol	789	352	514	8.1	24.6	1.69D
Iso-propanol	785	277	508	4.8	18.3	1.66D
n-Butanol	810	390	563	4.9	17.8	1.63D

^a At standard temperature and pressure (STP).

^b At sea level.

Table 2

Compositional analysis of sunflower husks used in this study (wt% wet basis).

Component	Method	Wt% (wet basis)
Dry matter	ASM013	91.78
Ash	ASM048	4.6
Protein	NA ^a	8.3
Fat (ether extract)	ASM044	0.55
Neutral detergent fibre (NDF)	ASM060	77.34
Acid detergent fibre (ADF)	NA ^a	65.18
Acid detergent lignin (ADL)	NA ^a	34.71
Cellulose	Calculated ^b	30.47
Hemicellulose	Calculated ^c	12.16
Lignin	ADL ^d	34.71

^a Method not accredited.^b Cellulose content = ADF–ADL.^c Hemicellulose content = NDF–ADF.^d Lignin content = ADL.

Dote et al., 1996). The autoclave has a working volume of 950 mL, an inside diameter of 90 mm, a height of 150 mm and is equipped with a high pressure stirrer and is heated with an electrical heating jacket.

Biomass (30 g) was liquefied with 70 mL solvent at a reaction temperature of 280 °C. Five different solvents were used (water, ethanol, methanol, iso-propanol and *n*-butanol). The holding time for all experiments was 30 min. The influence of temperature on biochar production was done with the solvent with the highest yield and the temperature was varied between 240 and 320 °C.

In a typical run, the autoclave was loaded with 30 g sunflower husks and 70 mL solvent and the autoclave was closed by tightening the lid using M10 Allen cap bolts. The oxygen (O₂) present in the reactor was purged three times using N₂ and then the pressure was increased to 10 bar using the gas chosen for preparation of the biochars. The reactor was then heated to the desired temperature and was maintained at that temperature for 30 min. Thermocouples were used to measure the temperature inside and outside the autoclave. In all experiments, the autoclave was agitated using a magnetic stirrer drive at 720 rpm to ensure homogeneous mixing. Upon completion of each experiment, the heating jackets were removed and the autoclave was allowed to cool to room temperature using an electric fan.

The autoclave was opened by unfastening the bolts after it had cooled down to room temperature to recover the liquefaction products. The same solvent that was used during liquefaction was used to dissolve all organic compounds in the crude extract in the autoclave while stirring. Biochar was recovered as a solid product by means of vacuum filtration using Whatman No. 3 filter paper to separate the solid residues and liquid. The solid residue was dried over night at 105 °C for 24 h to remove the remaining solvent and moisture. The dry biochar was then weighed and stored in a sealed container for further analysis. The biochar yield was calculated as the ratio of the mass of biochar obtained and the mass of sunflower husks used in the experiment.

2.4. Biochar analyses

2.4.1. Structural analysis

The physical–structural properties, including surface area, porosity, pore volume and pore diameter have been identified as having a significant impact on the utilisation processes of biochars (Guerrero et al., 2008; Apyadin-Varol and Putun, 2012). Brunner–Emmett–Teller (BET) surface areas and other parameters were determined for the feedstock and produced biochars via CO₂ adsorption multilayer theory using an Accelerated Surface Area and Porosimetry System.

Structural changes of the biomass and biochars were analysed using an FEI Quanta 250 FEG (Field Emission Gun) – ESEM (Envi-

ronment Scanning Electron Microscope) system in high vacuum mode. Scanning electron microscopy (SEM) is a potential technique to study the morphology of solid fuel particles. SEM analysis has been used especially to evaluate the structural variations in char particles after different thermal treatments. SEM images are very useful to obtain accurate details about the pore structure of biochars and the comparison between biochars and their raw materials would then allow for conclusions on morphological changes during the carbonisation stage to be drawn (Haykiri et al., 2001).

Structural analysis of the produced biochars were performed using Fourier transform infrared spectroscopy (FTIR) using an IRAffinity 1 spectrophotometer from Shimadzu (Japan). For observable adsorption spectra, fine dried biochar samples 3 mg were mixed with 97 mg of potassium bromide (KBr) using a pestle and mortar. The spectra were measured between 4000 and 600 cm^{−1}. FTIR analysis was used to examine functional groups on the surface of biochar samples and feedstock.

2.4.2. Compositional analysis

Proximate analysis was performed on the produced biochars using a thermo-gravimetric analysis (TGA) System from U-THERM (China). Proximate analysis helps to assess the weight percentages of volatile matter, fixed carbon, moisture and ash content in biochar and raw material samples (Donahue and Rais, 2009). Samples were heated up to 105 °C at a rate of 10 °C/min then up to 900 °C at a rate of 50 °C/min. Mass evolved at 105 °C was taken to be moisture, while mass evolved between 105 °C and 900 °C was taken to be volatiles. All mass remaining after heating to 900 °C consisted of fixed carbon and ash. Ash content was determined by the ARC Irene laboratories according to ASM standard methods (ASM048). Fixed carbon content was determined as the difference between 100% and the cumulated value of volatile matter and ash on a dry basis.

Elemental analysis was done following the ASTM D3176 standard method. The carbon (C), hydrogen (H) and nitrogen (N) content were measured directly using Elemental Vario EL cube elemental analyser and oxygen content was calculated by difference. The heating value of the biochars were determined following ASTM D5865 standard method, corrected for N and S content before conversion to a dry and ash-free basis.

2.5. Calculation of yields and recoveries

Biochar yield was calculated as the ratio of mass of biochar obtained to mass of sunflower husks used in the experiment. Lu et al. (2013) defined an Energetic retention efficiency that indicated what portion of the energy contained in the initial feedstock was retained in the biochar. In this study, this quantity was calculated as energy retention parameters (ERP) according to Eq. (1):

$$\text{Energy retention parameter} = \frac{\text{Energy content of biochar}}{\text{Energy content of feedstock}} \times \frac{\text{mass of dry biochar}}{\text{mass of dry feedstock}} \quad (1)$$

The energy retention parameter indicates the extent to which energy in the original biomass was retained in the biochar and is a better indication of the increase of the energy content of the biochar than only comparing an increase in higher heating value (HHV) because it is directly related to the amount of recovered dry biochar.

Energy densification is defined in this study as the ratio between the energy content of the produced biochars and the energy content of the feedstock.

3. Results and discussion

3.1. Biochar yield

The main role of the solvent in biomass liquefaction is to provide a medium for the decomposition of biomass and to provide active hydrogen. The presence of active hydrogen helps to stabilise liquefaction fragmented components and prevent the fragments from recombining to form complex compounds that are more difficult to decompose (Huang et al., 2011). Water is most often used as solvent in thermochemical liquefaction, because it is environmental friendly, relatively inexpensive and has a favourable critical temperature and pressure (Roman et al., 2012; Lu et al., 2012, 2013; Parshetti et al., 2013; Akhtar and Amin, 2011; Pinkowska et al., 2011). However, it has been reported that biomass liquefaction with water results in products with lower carbon content, a higher oxygen content and low heating value. The use of organic solvents have been adopted (Liu et al., 2013b, 2009; Huang et al., 2011) to enhance the yield of bio-oil with lower oxygen content and higher heating values. In this study, the thermochemical liquefaction of sunflower husks was studied at 280 °C with a biomass loading of 30 g kg⁻¹ solvent using distilled water, methanol, ethanol, isopropanol and *n*-butanol as solvents. The effect of using the different solvents on the dry biochar yield in a reducing (N₂) and a non-reducing (CO₂) atmosphere is presented in Fig. 1.

Liquefaction with methanol, ethanol and iso-propanol as solvent resulted in significantly higher biochar yields compared to water and *n*-butanol. Methanol, ethanol and iso-propanol have lower critical temperatures and pressures compared to water and *n*-butanol and thus, the more easily it is vaporised with an increase in temperature. At a temperature of 280 °C (18–25 MPa), water and *n*-butanol is in a sub-critical phase while ethanol, methanol and iso-propanol is in a super-critical phase. This explains why water and *n*-butanol resulted in lower biochar yields compared to the lower alcohols. During liquefaction, cellulose, hemicellulose and lignin is progressively hydrolysed with increasing temperature, with cellulose being the most difficult to decompose due to its crystalline structure (Toor et al., 2011). However, the higher solubility of the biomass in alcohols in the supercritical phase enabled the rapid depolymerisation of cellulose, hemicellulose and lignin through hydrolysis. Lignin was depolymerised and hydrolysed into phenolic compounds and alkyl-substituted phenols similar to what was reported by Kang and co-workers (2013) with more alkyl-phenol groups and less methoxyl aromatic groups forming at higher temperatures. These phenolic and methoxyl aromatic groups can repolymerise and condense to solid products (biochar). The low heating rate (2.5 K min⁻¹) afforded more time for repolymerisation

of decomposition products from especially lignin and this resulted in the high biochar yields observed in this study.

The influence of temperature on biochar yield was investigated in ethanol as solvent and N₂ and CO₂ as reaction atmosphere with a biomass loading of 30 g kg⁻¹ solvent. As expected from literature, the biochar yield decreases with an increase in temperature. It is interesting to note however that even at temperatures as high as 320 °C, there is still more than 450 g kg⁻¹ biochar present in the final product. This indicates how well ethanol manages to act as solvent for the liquefaction products and promote the formation of biochar even at high temperatures. This result shows that ethanol is a very attractive solvent for the production of solid biochar for a variety of applications. One of the negative aspects of organosolv thermochemical liquefaction has been the use of petroleum based solvents to affect oil or char formation. The good results obtained for ethanol shows the possibility of using bio-ethanol as solvent to make the overall production of biochar by thermochemical liquefaction more environmentally friendly.

The role of gas during hydrothermal liquefaction is to stabilise fragmented products and inhibit condensation, cyclisation and repolymerisation reactions that leads to the formation of biochar. In this regard, non-reducing gases such as hydrogen (H₂) and N₂ are favoured (Akhtar and Amin, 2011) for high bio-oil production from feedstock with a high cellulose and hemicellulose content. In this study, the lignin content of the feedstock is very high and thus it is expected that a reducing gas such as nitrogen will increase the possibility of recondensation and thus biochar formation. Nitrogen (reducing gas) consistently produced higher amounts of biochar in the presence of all solvents than carbon dioxide (CO₂) (non-reducing gas). The presence of CO₂ together with the higher solubility of the biomass in the alcohols led to increased interaction of the CO₂ molecules with the depolymerisation fragments and thus increased oil and gas production leading to lower overall biochar being formed. The difference in biochar yield is more pronounced at lower temperatures (<280 °C) than at higher temperatures. Structural analysis will show that at temperatures below 280 °C, the charring of the biomass has not been complete, with some of the cell wall lignin still intact.

The higher biochar yields at lower temperatures for N₂ compared to CO₂ thus lead to the conclusion that CO₂ is better at stabilising decomposition fragments at lower temperatures than N₂, leading to less char and more liquid products being formed. The temperatures used in this study resulted in no oil being formed, but only an organic liquid phase.

3.2. Structural analysis

3.2.1. Scanning electron microscopy (SEM)

SEM analysis was used to determine structural variations of raw biomass and biochar samples at different temperatures. Comparison of the SEM images of the biochars and raw material shows morphological changes occurring during liquefaction. The SEM analysis shows incremental increase in degradation of the plant material, but at temperatures below 280 °C, there was incomplete decomposition of biomass, and not all the plant material was charred. As the temperature increases, biomass decomposition increases and the underlying layers of the biomass become more exposed resulting in improved porosity of the biochar. Secondary layers, which include microfibrils, were exposed at 300–320 °C. Biochar samples from 280 to 320 °C had several cracks and holes, and this was due to the evolution of volatiles as the temperature was increased. According to Haykiri et al. (2001), the level of devolatilisation has a significant influence on the properties of the resultant chars. With increasing temperature, biochars produced in this study showed a more porous surface which was confirmed by BET analysis.

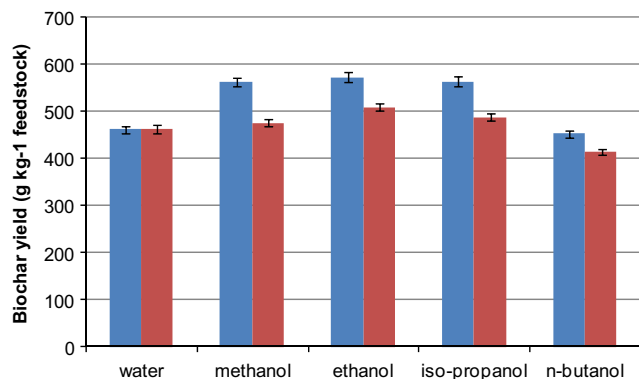


Fig. 1. Influence of solvent on biochar yield in N₂ (■) and CO₂ (■) atmosphere.

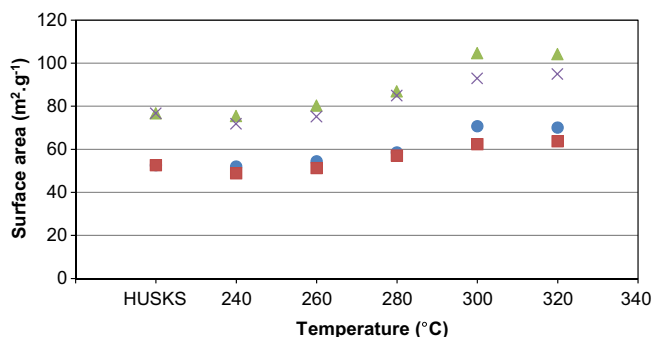


Fig. 2. Surface area at different temperatures for sunflower husks and biochar samples under N_2 and CO_2 atmospheres (▲ – D-R micropore surface area in CO_2 , X – D-R micropore surface area in N_2 , ● – BET surface area in CO_2 , ■ – BET surface area in N_2).

3.2.2. Brunauer–Emmett–Teller analysis

Surface area was determined with CO_2 adsorption using BET porosimetry analysis and the results are shown in Fig. 2.

As expected, the surface area increased with increasing temperature as volatiles was liberated from the biomass. It has been shown by SEM analysis that chars at 240 and 260 °C still contain significant amounts of biomass material and this can be seen in the relatively little change in surface areas of the chars compared to that of the husks at these temperature. There was a significant increase in biochar yield with temperature for temperatures higher than 280 °C which is in agreement with SEM analysis that shows increased exposure of the plant material as well as increased decomposition of the solid material and deposition of condensation products. In all instances, CO_2 produced biochars with a higher surface area than N_2 . This can be attributed to the relatively higher interaction of CO_2 with the biomass material and decomposition fractions that leads to the formation of oils and gas, resulting in a larger amount of small pores in the biochar. The surface areas are low compared to that of activated carbon ($\sim 500 \text{ m}^2 \text{ g}^{-1}$) indicating that additional preparation is necessary if the chars are to be used for the production of activated carbon or as carrier for catalysts.

3.2.3. FTIR analysis

The FTIR spectra were obtained for sunflower husks and biochars prepared with ethanol as solvent in a N_2 and CO_2 atmosphere. The most prominent peaks observed in the spectra for both gases are presented in Table 3.

The spectra for the biochars prepared in the different atmosphere have the same common peaks although some peaks

are more pronounced for biochars prepared in N_2 than for biochars prepared in CO_2 . The peaks present in the biomass at a wave number of 3800 cm^{-1} , 3680 cm^{-1} and 3360 cm^{-1} either disappears with an increase in temperature or the peaks becomes broader as temperature increases, suggesting that the dehydration of cellulose progresses more severely with increasing liquefaction temperatures. The fact that these peaks are still present might indicate that the cellulose structures have not completely decomposed even at 300 °C. It also indicates an increase in hydrophobicity of the biochars with an increase in temperature, indicating a higher resistance to humidity when stored (Liu et al., 2013a,b). The peak observed at 2920 cm^{-1} is present in the husks, but disappear completely with increasing temperature while the peak observed in the husks at 2360 cm^{-1} becomes more pronounced with an increase in temperature. This phenomenon indicates the disappearance of symmetric aliphatic groups and the appearance of asymmetric aliphatic groups and hydro-aromatics. This is an indication of aromatic compounds formed due to condensation and cyclisation reactions of decomposition fragments with increasing temperature. This is supported by an increase in peaks at 1600 cm^{-1} , 1700 cm^{-1} and the appearance of peaks at 740 cm^{-1} that all indicate the formation of aromatic compounds as the lignocellulose is decomposed. The disappearance of peaks at between 1560 and 1160 cm^{-1} is indicative of the decomposition of cellulose through dehydration and hemicellulose and lignin through dehydration and carboxylation. The peak at 1060 cm^{-1} is normally associated with the $O-CH_3$ stretching in lignin (Liu et al., 2013a,b). It is interesting that the peak disappears at 260 °C, indicating decomposition of lignin, but reappears at 280 and 300 °C. This could suggest rearrangement of the methoxyl groups on the lignin structure to aromatics, but there is no evidence of the groups present to support this claim.

3.3. Compositional analysis

The results of proximate and elemental analysis on the sunflower husks and produced biochars are presented in Table 4.

The proximate analysis shows a decrease in volatile matter and an increase in fixed carbon content with an increase in temperature. This is expected since the husks is degraded more at higher temperatures, resulting in more volatile matter released and condensing to form biochar. There is no significant difference in composition between biochars prepared in N_2 or CO_2 . The ash content in both atmospheres is increased almost two fold with an increase in temperature, which signifies a decrease in combustibles in the biochars, which is consistent with results obtained by Lu et al. (2012) and is also consistent with a decrease in S content. The increase in N content with temperature correlates with the peak formed at 750 cm^{-1} on the FTIR spectra for both atmospheres

Table 3

Identification of prominent peaks on FTIR spectra of biochars prepared at different temperatures and in either a nitrogen or carbon dioxide atmosphere.

Wave number	Characteristic vibration	Reference
3800–3040	–O–H stretching associated with free and bonded vibration most often associated with cellulose	Parshetti et al. (2013), Keiluweit et al. (2010), Liu et al. (2013a)
2920	–C–H stretching of symmetric aliphatic –CH ₃	Keiluweit et al. (2010)
2880	–C–H stretching of asymmetric aliphatic –CH ₂	Roman et al. (2012)
2360	Aliphatic –C–H and C=O vibrations	Parshetti et al. (2013)
1700–1600	–C=C and C=O vibrations associated with carboxyl, aldehyde, ketone, ester and conjugated aromatic groups	Parshetti et al. (2013) Sevilla and Fuertes, (2009), Keiluweit et al. (2010)
1560–1480	–C–H stretching associated with lignin and cellulose	Parshetti et al., (2013)
1400–1240	–C–O ether vibration	Das et al. (2009)
1160–1180	–C–O–C stretching in lignocellulose	Parshetti et al. (2013)
1060–960	–C–O stretching and O–CH ₃ vibration in lignin	Liu et al. (2013a)
860	Associated with polycyclic aromatic structures	Biniak et al. (1997)
740	Aromatic C–H vibrations	Parshetti et al. (2013)

Table 4
Proximate and elemental analysis of sunflower husks feedstock and produced biochars at different temperatures. All values are given on an oven-dry basis and in weight percentage.

N ₂	VM %	FC %	Ash %	N %	C %	H %	S %	O %	HHV ^c (MJ/kg)	ED ^a	ERP ^b	H/C	O/C	(O + N)/C
Husks	52.6	15.7	8.4	1.94	49.03	6.17	0.33	42.53	19.9	–	–	0.13	0.87	0.91
240 °C	50.8	32.7	5.2	2.21	52.43	5.67	0.19	39.50	19.7	1.0	0.62	0.10	0.75	0.80
260 °C	47.1	34.9	8.7	2.03	51.18	5.29	0.11	41.39	18.7	0.9	0.56	0.10	0.81	0.85
280 °C	45.0	38.8	9.0	2.25	53.87	4.91	0.06	33.91	21.8	1.1	0.54	0.08	0.58	0.61
300 °C	41.4	42.8	10.9	2.44	60.58	5.23	0.09	31.66	23.0	1.2	0.53	0.09	0.52	0.56
320 °C	39.0	47.1	10.9	2.64	64.58	5.29	0.10	27.39	26.1	1.3	0.59	0.08	0.42	0.47
CO ₂														
240 °C	63.01	30.1	6.8	1.80	54.46	5.89	0.08	37.47	20.8	1.0	0.58	0.11	0.69	0.72
260 °C	61.0	31.6	7.5	1.99	55.58	5.80	0.05	36.58	21.2	1.1	0.59	0.10	0.66	0.69
280 °C	50.8	40.1	9.2	2.20	57.57	5.37	0.03	34.83	21.7	1.1	0.56	0.09	0.61	0.64
300 °C	41.4	48.8	9.8	2.74	66.25	5.32	0.10	25.59	25.7	1.3	0.59	0.08	0.39	0.43
320 °C	38.6	48.9	12.4	2.63	65.45	5.33	0.11	26.43	26.8	1.3	0.60	0.08	0.40	0.44

^a Energy densification.

^b Energy retention parameter.

^c HHV = 0.352C + 0.944H + 0.105 (S–O) (Channiwalla and Parikh, 2002).

which can be attributed to the formation of pyridine at higher temperatures. The HHV increased for all biochars compared to the sunflower husks. This is consistent with the increase in fixed carbon content, but the final HHV is low compared to low grade coal in South Africa (approximately 29 MJ kg^{−1}). The energy density is increased for both atmospheres with an increase in temperature, indicating the densification of the biomass as the fixed carbon content of the material is increased. The energy retention parameter stayed approximately the same, but the average retention of energy in the biochars was found to be 55% for biochars prepared in N₂ and 58% for biochars prepared in CO₂. Energy wise, this means that CO₂ performed better in retaining the energy in the biochar than N₂ had, even though the chemical composition of the biochars prepared in the two atmospheres is approximately the same. The decrease in O/C and (O + N)/C ratios indicates an increased hydrophobicity of the biochars, consistent with the formation of more aromatic compounds as was evidenced by the FTIR analysis of the biochars.

The H/C and O/C ratios obtained for biochars in this study is compared to H/C and O/C ratios obtained by other researchers with similar feedstock on a Van Krevelen diagram (see Fig. 3).

The biochars prepared in this study from sunflower husks in ethanol as solvent within a CO₂ atmosphere is closest to coal on the Van Krevelen diagram, indicating that these chars would be excellent sources of carbon for co-gasification. The low S content of the chars observed with elemental analysis indicate that these

chars would lower the overall greenhouse gas emissions when co-gasified with coal.

4. Conclusions

Lower alcohols produced higher biochar yields which could be attributed to their good solubility properties to depolymerise plant material, leading to the formation of more aromatic compounds and condensation to solids. Porosity, surface area and fixed carbon content increase and volatile matter decrease with an increase in temperature, with chars prepared in CO₂ having the closest relation to coal on a Van Krevelen diagram. CO₂ performed better than N₂ in retaining the energy of the feedstock in the char. It can be concluded that biochar produced through thermochemical liquefaction in ethanol would be ideally suited to co-gasification with coal.

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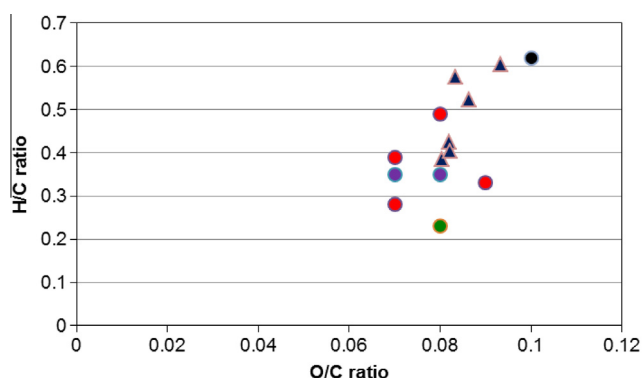


Fig. 3. Van Krevelen diagram for sunflower husk based biochars from this study compared to that obtained for similar feedstock by other researchers (● – chars derived from coconut fibre and eucalyptus (Liu et al., 2013a,b), ● – chars derived from paper and wood (Hwang et al., 2012), ● – Chars derived from corn stalks (Xiao et al., 2012), ● – coal (Parshetti et al., 2013), ▲ – this study).

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